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# (54) IMPROVEMENTS IN OR RELATING TO CHEMICAL COMPOUNDS HAVING JUVENILE HORMONE ACTIVITY

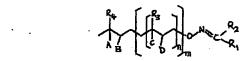
(71) We, A/S CHRMINOVA, a company organized under the laws of Denmark, of 7620 Lemvig, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to chemical compounds having juvenile hormone activity. More particularly, the present invention relates to methods and compositions for the control of insects, and to alkyl, terpenoid and olefinic oximethers of some aryl, pyridyl and aliphatic aldehydes and ketones.

Some compounds exhibit high juvenile hormone activity when applied topically to the insect; stimulating its development and preventing formation of sexually mature adults. Compounds exhibiting this activity may be envisaged as potential insecticides of the third generation.

The compounds of the present invention act selectively on certain insects and, moreover, exhibit high sterilizing properties. The compounds are cheap to prepare and possess higher activity for some insects than many known compounds.

The novel compounds of the present invention are oximethers represented by the following general formula (I)



in which the symbols represents,

A: hydrogen or an alkyl group or an alkoxy group,

B: a hydrogen atom, or,

AB: when taken together, a further single bond between the adjacent carbon atoms,

or an oxygen atom,

C: a hydrogen atom,
D: a hydrogen atom, or,
CD: when taken together, a further single bond between the adjacent carbon atoms,

n: zero or one,
m: zero or one,

R<sub>4</sub>: a methyl or ethyl group,
R<sub>5</sub>: a methyl or ethyl group,
R<sub>7</sub>: a hydrogen atom, or an alkyl group with from 1 to 6 carbon atoms,

an alkyl group, a hydroxy group, a hydroxyalkyl group (e.g. —CH<sub>2</sub>OH or —C<sub>2</sub>H<sub>4</sub>OH), an alkoxy group, an alkoxyalkyl group (e.g. —CH<sub>2</sub>—O—CH<sub>3</sub>), a carboxy group, a carboxyalkyl group (e.g. —CH<sub>3</sub>—COOH), a carbalkoxy group i.e., —COOR where R is an alkyl group, a carbalkoxyalkyl group (e.g. —CH<sub>2</sub>COOR, where R is an alkyl group), a mono-, di- or tri-halogenalkyl group, an amide group, a 3,4-methylenedioxyphenyl group, or the group with the general formula (II)

[Price 33p]

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 $(\Pi)$ 

wherein Z is CH or a nitrogen atom, p is 0 to 3, and X is hydrogen or a substituent such as, for example, NO2, halogen, OH, CF2, an alkyl group or an alkoxy group, which substituent X, when p is 2 or 3 may be the same or different.

In all the above definitions, the alkyl, halogenalkyl and alkoxy groups preferably each contain from 1 to 6 carbon atoms. The alkyl is said groups, including the haloalkyl and alkoxy groups, may be straight or branched. As examples may be mentioned methyl, ethyl, propyl, i-propyl, t-butyl, pentyl and hexyl. Preference is given to methyl and ethyl. Preferred compounds of the present invention are compounds of the general formula (I), in which the symbols represents,

A: hydrogen or an alkyl group or an alkoxy group with 1 to 2 carbon atoms

a hydrogen atom, or,

AB: when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,

a hydrogen atom, D: a hydrogen atom, or,

CD: when taken together, a further single bond between the adjacent carbon atoms,

n: zero or one, m: zero or one,

a methyl or ethyl group,

R: a methyl or ethyl group, R,: a hydrogen atom,

R<sub>2</sub>: a carbalkoxy group (—COOR, where R is an alkyl group with from 1 to 6 carbon atoms), a carbalkoxyalkyl group (e.g., —CH<sub>2</sub>COOR, where R is an alkyl group with from 1 to 6 carbon atoms), a 3,4-methylenedioxyphenyl group, or

a group with the general formula II, wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH<sub>0</sub>, when p is one.

Another preferred range of compounds are compounds of the general formula I, in which the symbols have the following meanings: 30

A: a hydrogen atom,

a hydrogen atom, C: a hydrogen atom, and

a hydrogen atom, or

CD: when taken together, a further single band between the adjacent carbon atoms, 35 n: zero or one,

m: zero or one,

(ÍV),

a methyl or ethyl group, R: a methyl or ethyl group,

40 R: a hydrogen atom, carbalkoxy group, a carbalkoxyalkyl group, a 3,4-methylenedioxyphenyl group, or a group having the general formula (II) wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH<sub>4</sub>, when p is one.

The compounds of the general formula (I) may be prepared, for example, by the following processes: a) By etherformation (O-alkylation) between a compound of the general formula

(III)

wherein A, B, C, D, n, m, R, Rs, Rs, and Rs have the same meaning as mentioned above and Hal. is chlorine, bromine or iodine.

b) By epoxydation of a compound of the general formula (III b) to form a compound

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of the general formula (III bb), followed by an etherformation according to process a) to form a compound of the general formula (I b)

(III b) epoxydation 
$$\stackrel{R_{\psi}}{\longleftrightarrow} \stackrel{\stackrel{R_{3}}{\longleftrightarrow}}{\longleftrightarrow} \stackrel{Hal}{\longleftrightarrow} \stackrel{R_{\psi}}{\longleftrightarrow} \stackrel{\stackrel{R_{3}}{\longleftrightarrow}}{\longleftrightarrow} \stackrel{Hal}{\longleftrightarrow} \stackrel{Hal}{\longleftrightarrow} \stackrel{Hal}{\longleftrightarrow} \stackrel{R_{\psi}}{\longleftrightarrow} \stackrel{R_{$$

(III bb) + (IV) 
$$\xrightarrow{\text{base}}$$
  $\xrightarrow{R_1}$   $\xrightarrow{R_2}$   $\xrightarrow{R_3}$   $\xrightarrow{R_2}$   $\xrightarrow{R_2}$   $\xrightarrow{R_3}$   $\xrightarrow{R_2}$   $\xrightarrow{R_3}$ 

c) By alkoxylation of a compound of the general formula (III b) to form a compound of the general formula (III c), followed by an etherformation according to process a) to form a compound of the general formula (I c) 5

(III b) 
$$\frac{1 \left\{ \begin{array}{c} Hg(2)\text{-salt} \\ R_0OH \end{array} \right\}}{2 \text{ NaOH}_bNaBH_4} \xrightarrow{R_4} \left( \begin{array}{c} R_3 \\ R_2OH \end{array} \right) \xrightarrow{R_4} \left( \begin{array}{c} R_3 \\ R_3OH \end{array} \right)$$

$$(\text{III c}) + (\text{IV}) \xrightarrow{\text{base}} \qquad \qquad \begin{matrix} \varrho_{1} \\ \varrho_{2} \\ \vdots \\ \varrho_{r} \end{matrix} \qquad \qquad \begin{matrix} \varrho_{2} \\ \varrho_{1} \\ \vdots \\ \varrho_{r} \end{matrix}$$

	(I c)	
10	wherein R <sub>s</sub> is an alkyl group with from 1 to 6 carbon atoms.  Variations in these main processes due to variation in the starting material may	10
4.	d) Process a), when A B taken together represent a single bond, C D taken together represent a single bond, n is one and m is one.	
15	e) Process a), when A B taken together represent a single bond, C is hydrogen, D is hydrogen, n is one and m is one.	15
00	f) Process a), when A B taken together represent a single bond and m is zero.  Process a), when A B taken together represent a single bond, n is zero and m is one.  Process b), when C D taken together represent a single bond, n is one and m is	
20	i) Process b), when C is hydrogen, D is hydrogen, n is one and m is one. j) Process b), when m is zero.	20
	k) Process b), when n is zero and m is one.  1) Process c), when C D taken together represent a single hand, n is one and m is one.	
25	n) Process c), when m is zero. o) Process c), when m is zero. o) Process c), when n is zero and m is one.	25
	The reaction according to process a) between a compound of formula (III) and a compound of formula (IV) is preferably performed in the presence of a beauty in the presenc	
30	amide.	30
	The oximethers of formula (I) can, for example, be prepared according to this process from the chloride, bromide or iodide of the compound of formula (III) by reacting it with a 10% malor excess of the compound of formula (III) by	
35	reacting it with a 10% molar excess of the appropriate oxime of formula (IV) and powdered KOH in dimethylformamide. The reaction mixture is stirred for 3 to 20	35

hours at a temperature between 20 and 60°C, then diluted with water and extracted with ethylether. The organic extract is washed with a 10% KOH solution and finally washed with water. The extract is then dried over anhydrous NaSO<sub>4</sub>, and the solvent is removed in vacuo. The resulting crude oximether is purified by column chromatography on silien call prints a house a debut operation relative in organization. tography on silica gel, using a benzene/ethylacetate mixture in graduent clution.

	The purity can be established to 99% by GLC and combined spectrometric	
	methods.  The epoxydation process according to b) is preferably performed with m-chloro-	
5	perbenzoic acid as the epoxidation agent.  The compounds of formula (III b) can, for example, be epoxidized by reaction	5
	with m-chloroperbenzoic acid in methylenechloride at 0 to 5°C for two hours. A 10% molar excess of the peracid is used. After the epoxidation is completed, the reaction mixture is poured into an ice-cold 10% aqueous NaHCO <sub>2</sub> solution and is shaken thoroughly. The organic layer is then washed with water, dried over anhydrous Na <sub>2</sub> SO <sub>4</sub> ,	
10	and the solvent is removed in vacuo.  The epoxy halogenide of formula (III bb) thus formed is reacted with an oxime of formula (IV) according to process a) as described above, to form a compound of	10
	the general formula (I b).	
15	In process c), the terminal alkoxylated compounds of the general formula (I c) can be prepared by the oxymercuration procedure of Brown, H.C. et al.: (J.A.C.S., 91, 5646, (1969)).	15
	The alkenes of formula (III b) are, for example, treated with mercuric acetate in the appropriate alcohol i.e. the alcohol of formula R <sub>2</sub> OH, resulting in the desired alkoxy	
20	group in the end product, and the resulting oxymercuric intermediate is reduced by adding a solution of NaBH, in aqueous NaOH. The mixture is stirred for two hours, until the mercury has coagulated and settled. The reaction product is extracted with n-hexane, the extract washed with water, dried over anhydrous Na <sub>2</sub> SO <sub>4</sub> , and the solvent	20
	removed in vacuo. The resulting alkoxylated halogenides of formula (III c) are reacted	
25	with oximes of the general formula (IV) according to process a) to form the terminal alkoxylated compounds of the general formula (I c).  The starting materials, oximes of the general formula (IV), may be made by	25
	standard methods from the appropriate carbonyl compounds and hydroxylamine hydrochloride.  The starting materials, halogenides of formula (III b), can, when n=n=1, be	
30	either geranylbromide or -chloride, or citronellylbromide or -chloride. The halogenides of formula (III b) with shortened chain-length, e.g. $n=m=0$ or $n=0$ and $m=1$ , are made according to the reaction schemes below.	30
	The Marc Julia synthesis. (Bull. Soc. Chem. France, 1072, (1960))	
35	RMyBr R HBr R Br	35
	R = methyl or ethyl. (Belg. patent No. 725 576)	
	R CHECK/Na/NHy R BIBUSON R PBY	
	R ar	
40	R = methyl or ethyl. or, according to Germann patent No. 1 117 107	40
	NCI R	
	R = methyl or ethyl.	
4	All chemical structures are confirmed by a combination of infrared and nuclear magnetic resonance (IR and NMR) data.	
45	In accordance with the present invention, there is provided a method for the control of insects, which comprises contacting the insects, or their eggs or larvae, with a compound selected from those of formula (I) in an amount effective to inhibit the metamorphosis of said insect or to act as sterilizing or ovicidal agent.	45
50	Said compound have found to act on species of different orders all over the class	
50	of insects, viz. Coleoptera (beetles, weevils), Lepidoptera (butterflies, moths), Hemip-	50

	1,419,000	5
	tera (bugs, plant lice, scales), Orthoptera (grass hoppers), Dictyoptera (roaches), and Diptera (flies, mosquimes).	
5	Accordingly, the invention also includes a composition containing a compound of the general formula (I) and a suitable carrier, which composition is suitable for the control of insect pests. To achieve a uniform distribution or application, it is advantageout to employ a composition comprising an inert corrier and on the control of th	.5
	One method for the control of insects in accordance with the present insection is	
10	to apply the composition comprising an inert carrier and a compound of formula (I) to the locus of insect infestation, such as to the plant life on which insects live. These composition can be either solid or liquid.  Solid composition for treating income	10
15	Solid composition for treating insects can be prepared by incorporating the active ingredient with an inert carrier such as finely divided tale, silica pyrophyllite, diatomite or clay or granular inert carriers, such as the vermiculites.	
	Liquid compositions can be prepared by mixing the active compound with inert carriers, such as acctone, xylene, peanut oil, cotton-seed oil, sesame oil and other vegetable oils and mineral oils conventionally employed as carriers in insecticidal formulation for application by spraying. Emplisions containing the active ingredient can also be used.	15
20	Other ingredients can be present in the composition of the present invention to aid in the effective application of the active ingredient, such as wetting agents, dispersing agents, insect attractums and the like.  The concentration of active ingredient of a concentration of active ingredient of active ingredient of a concentration of the present invention to aid	20
25	The concentration of active ingredient of a compound of formula I in the composition can vary depending on a variety of factors, such as the specific insect involved, the degree of insect infestation, the locus of insect infestation, environment and weather conditions, and type of application device used.	25
	Generally, the composition will contain less than 95% by weight of the active ingredient and more frequently less than 10% by weight.	
30	The compounds of formula (I) are useful insect control agents by virtue of their ability to inhibit the metamorphosis of said insect. The expression "to inhibit the metamorphosis of said insect" as used herein, and in the appending claims, is used to describe the direct effect of the compounds of formula (I) as well as the indirect insecticidal effects of said compounds	30
35	The compounds of formula (I) inhibit metamorphosis of various insect species at different stages, resulting in non-viable intermediates. Depending on the time of application, the compounds of formula (I) show ovicidal, larvicidal or pupicidal effect. When applied to the adult insect, the effect is indirect in the sense that the insect products non-viable eggs.	35
	The following examples are presented to illustrate the present invention.	
40	Etherformation.  Preparation of benzaldoxime-O-geranyi ether.	40
45	(85%) in 200 ml. dimethylformamide is stirred for 30 min. 34,6 g. (0,2 mol) geranyl-chloride is added and the reaction mixture is stirred over night at 50—60°C. 200 ml. water is added to the reaction mixture, which is then extracted with ether. After separation the organic layer is washed with 10% KOH and with water until neutral. The	45
50	n <sub>0</sub> <sup>34</sup> : 1,5202.	50
	Epoxidation.  Preparation of benzaldoxime-O-epoxygeranyl ether.  To a stirred chilled relation (2007)	
55	To a stirred, chilled solution (0°C) of 3,4 g. geranylchloride in 100 ml. methylene- chloride is cautiously added 4,5 g. (0,022 mol) 85% m-chloroperbenzoic acid in 30 ml. methylenechloride. The reaction mixture is stirred on an ice-bath for 2 hours, 10% aqueous NaHCO <sub>4</sub> solution is added and the mixture shaken thoroughly. The aqueous layer is extracted with methylenechloride and the season of the season o	55
60	layer is extracted with methylenechloride and the combined extracts evaporated in vacuo. The residue is dissolved in ether, washed twice with 10% NaHCO <sub>2</sub> solution and finally twice with water. The etheral extract is dried over anhydrous Na <sub>2</sub> SO <sub>4</sub> and evaporated in vacuo. 1,9 g. (0,01 mol) of crude 6,7-epoxygeranylchloride thus obtained is reacted with 1,2 g (0,01 mol) benzaldoxime in 10 ml. DMF in the presence of 0,7 g. KOH, according to the etherformation described above. For the actual oximether was found, n <sub>D</sub> **: 1,5255.	60

<u> </u>	Example 3.	
<b>.</b> 5	Alkoxylation.  Preparation of benzaldoxime-O-(7-ethoxy-geranyl)-ether.  3,4 g. geranylchloride (0,02 mol) is added to a vigorously stirred suspension of 6,4 g. mercuric acetate in 30 ml. of 99% ethanol at 0°C. One hour after the addition of the diene the mercurial intermediate is reduced by adding 20 ml 0,5 M NaBH, in	5
10	3 M NaOH. The mixture is allowed to stir for two hours, until the mercury has coagulated and settled. Then the product is extracted with n-hexane, washed with water until neutral, dried over Na <sub>2</sub> SO <sub>4</sub> and the solvent is removed in vacuo. 1,1 g. (0,005 mol) of crude 7-ethoxy-geranylchloride thus obtained is reacted with 0,6 g. (0,005 mole) benzaldoxime in 5 ml. DMF in the presence of 0,35 g. KOH, according to the etherformation described above. For the actual oxime ether was found, n <sub>D</sub> <sup>st</sup> : 1,5225.	10
	Example 4.	
15	Chromatography.  10 g. crude benzaldoxime-O-geranylether is purified by column chromatography on silica gel (0,2—0,5 mm.). The column is filled with 250 g. silica gel and a benzene/	15
20	benzene/ethylacetate (200 ml.), and then gradually increasing the concentration of ethylacetate during the clution: 3/1 (200 ml.), 7/3 (400 ml.), 3/2 (300 ml.) and finally 1/1 (200 ml.). The same procedure was applied to all other compounds.	20
	Example 5.	
٠.	Formulation.  The active ingredient prepared according to Example 1 can be formulated in the following way:	
25	Active ingredient 10,0 grammes 70% Ca-dodecylphenylsulfonate 5,0 5 Oleyl-poly(15)ethyleneoxide ether 5,0 5 Acetone ad 100 milliliters (100 g/l a.i.)	25
30	When poured into water, an emulsion is immediately formed, which shortly after is transformed into a true solution. Further dilution into any desired concentration can be performed.  The water based solution is ready for spraying.	30
35	In a similar manner to that used in the examples given above, the following compounds were also prepared.	35

### TABLE 1

Comp. No.	Formula and name	n <sup>24</sup>
. 1	Benzaldoxime-O-geranyl ether.	1,5202
2	Benzaldoxime-0-6,7-propoxygeranyl ether.	1,5255
	- Components	
3	Benzaldoxime-O-(7-ethoxy-geranyl)-ether.	1,5225
	\$ 100 mg	
4	Benzaldoxime-O-(3-ethyl-7-methyl-2,6-nonadiene-1-yl)-ether.	1,5196
5	Piperona loxime-O-gerany! ether.	1,5312
	Lungtis>	
6	p-Tolualdoxime-O-geranyl ether.	1,5233
7	3-Pyridinealdoxime-O-geranyl ether.	1,5350
		,
8	Benzaldoxime-O-citronellyl ether.	1,5206
		<u>-</u>

TABLE 1	(Continued)
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	TABLE I (Continued)	
Comp. No.	Formula and name	n24 D
9	Piperonaloxime-O-(3-methyl-2-pentene-1-yl)-ether.	1,5596
10	Benzaldoxime-O-(3-methyl-2-pentene-1-yl-)-ether.	1,5363
11	Piperona loxime-O-(4-methy 1-3-hexene-1-y1)-ether.	1,5500
	20000	
12	Benzaldoxime-O-(4-methyl-3-hexene- 1-yl)-ether.	1,5303
13	Glycollicaldoxime-O-geranyl ether.	1,4905
• •	- And Andrews	
14.	Glyoxylic acid ethylester aldoxime-O- geranyl ether	1,4682
	Lowin	
15	Glyoxylic acid ethylester aldoxime-O- (epoxygeranyl)-ether.	1,4706
	- Nonion	

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#### TABLE 1 (Continued)

Comp. No.	Formula and name	n <sup>24</sup> D
16	Glyoxylic acid ethylester aldoxime-O- (7-ethoxy-geranyl)-ether	1,4702
	~ in	
17	Glyoxylic acid ethylester aldoxime-Ocitronellyl ether	1,4713
18	Glyoxylic acid ethylester aldoxime-O- (7-methoxy-citronellyl)-ether	1,4722
	offenda	
19	Glyoxylic acid ethylester aldoxime-O- (3,7-dimethyl-octyl)-ether	1,4453
	→ Loon Loon	

Testing of juvenile hormone activity.

The biological tests are examplified by tests on Tenebrio molitor L., Galleria mellonella L. and Culex pipiens L. Tenebrio test: The material in question is applied topically to the abdomen of 0,5 to 2 hours old pupae of the said specimen, as a solution in acctone. The pupae are held at 27°C and 70% RH, ecdysis occurring 5 to 7 days later. The degree of inhibition of adult characters is referred to an arbitrary scale, a morphologically perfect adult given the character 0%, a perfect second pupa 100%.

Galleria Test: The test is performed on recently laid eggs of Galleria mellonella by contact with impregnated filter paper. The data given in table 2, are the amount necessary for preventing eclosion of 50% of the eggs. The amount (IC—50 eclos.) is given in mg./65 cm².

given in mg /65 cm<sup>3</sup>.

Culex test: The compounds were tested on mature larvae of Culex pipiens. The concentration necessary to produce a loss of 50% of the test animals is given in table 2. (IC-50 eclos.) in ppm.

TABLE 2

Comp. No.	Tenebrio test ID-50 morph. µg./pupa	Galleria test IC-50 eclos. mg/65 cm²	Culex test IC-50 eclos. ppm
1	0,05	>10	<1,0
2	>0,1		-
3	1,0	10	10
4	0,01	-	-
5	>100	10	1,0
6	50	1,0	10
7	10	_	-
8	>100	10	<10
9	10	10	0,02
10	>100	1,0	1,0
11	>100	5	0,5
12	>100	1,0	₫0
13	.50	-	10
14	1	-	1,0
15	1	-	1,0
16	· 1	1	1,0
17	-	1,0	-
18	***	1,0	-

All compounds made and tested are mixtures of isomers.

#### WHAT WE CLAIM IS:—

1. A novel chemical compound corresponding to the general formula-I

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I

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in which the symbols have the following meanings:

A: hydrogen or an alkyl or alkoxy group, and

B: a hydrogen atom, or

AB: when taken together, a further single bond between the adjacent carbon atoms, or

an oxygen atom,

C: a hydrogen atom, and

D: a hydrogen atom, or CD: when taken together, a further single bond between the the adjacent carbon atoms,

<ul> <li>n: zero or one,</li> <li>m: zero or one,</li> <li>R<sub>i</sub>: a methyl or ethyl group,</li> </ul>	
m: zero or one,	
R.: a methyl or ethyl grown	
R: a methyl or ethyl group.	
5 R <sub>1</sub> : a hydrogen atom, or an alkyl group having	from 1 to 6 carbon atoms, 5
An alkyl group, (a hydroxy group, a hy	droxvalkyl group, an alkovy group, an
alkoryalkył group, a carboxy group, a	Carboxvalky group a carbally are constant
a caroaikoxyaikyi group, a mono-, d	- Of tri-halogenalkyi group on omide
group, a 3,4-methylenedioxyphenyl	group, or a group having the general
10 formula II	10
	II
<u> 7 Al-</u>	K. ***
	•
· · ·	
wherein Z is CH or a nitrogen gram	mata Aran and a series of
or at least one substituent which wi	p is 0 to 3, and X is a hydrogen atom
	en p is 2 or 3, may be the same or
<ol> <li>2. A novel chemical compound corresponding</li> </ol>	o to the general faculty .
to and the same of	g w me general formula I
	•
K*   [K 7]	o. I
	N R2
الد ا في الله	R.
ב רַיַּטּיַאָת	· · · · · · · · · · · · · · · · · · ·
in which the symbols have the following meanings	
A: an alkyl or alkoxy group, and	<b>;</b>
B: a hydrogen atom, or	•
20 AB: when taken together, a further single bond	hotmoon sho adiases, as to a second
an oxygen atom.	between the adjacent carbon atoms, or 20
C: a hydrogen atom, and	
D: a hydrogen atom, or	
CD: when taken together, a further single bond	between the adjacent carbon atoms
. 25 ". 15 ZEIU DI ONE.	25
m: is zero or one,	٠ .
R.: a methyl or ethyl group,	
R: a methyl or ethyl group,	
R <sub>i</sub> : a hydrogen atom, or an alkyl group having f	rom 1 to 6 carbon atoms,
30 - an anky group, a nyuroxy group, a hyd	DXValkyl group, an alboyy oroun an 20
arevelously in Californ and in the californ an	REDOXVALEU GUNDO a carbolleous coosso
a carbalkoxyalkył group, a mono-, di	or tri-halogenalkyl group, an amide
group, a 3,4-methylenedioxyphenyl grou or a group having the general formula II.	P,
35 3. A compound as claimed in claim 1 or cla	Car mark and
35 3. A compound as claimed in claim 1 or cla	im 2 in which the symbol X represents 35
any of the following atoms or groups NO <sub>2</sub> , hale 4. A compound as claimed in claim 1 or 2	gen, Uri, Cra, alkyl and alkoxy.
halogenalkyl or alkoxy represented by the symb	of 5, in which any of the groups alkyl,
carbon atoms.	way w's sing we contains from 1 to 9
40 5. A compound as claimed in claim 1 or cl	aim 2 in which a hydromali-d arms
represented by We is any of the Stoling — ( )H ( )H	andC.H OH as all second based according
- Abanania of ve in the break and the company	. A CHINGING CONTO PRIVACENTAL by
Na is the group — Ch.Court, and a carballow	TOT COTTO LEON TO LEVEL COMMON COMMON COMMON AND COMMON
by K <sub>2</sub> is any or the groups — COOK andC	LCOOR, wherein R is an alkel aroun
45 TIMATINE I TO O CALDON SIDMS.	A5
6. A novel compound corresponding to the	general formula I in claim 1. in which
or symbols use for totowing meanings.	
A: an alkyl or alkoxy group having 1 or 2 carbo	atoms, and
B: a hydroben atom, or	
50 AB: when taken together, a further single bond	between the adjacent carbon atoms, or 50
an oxygen atom,	***************************************
C: a hydrogen atom, and	
D: a hydrogen atom, or	
CD: when tagen together, a further single bond	between the adjacent carbon atoms,

12	1,419,080	
	n: zero or one,	
	m: zero or one,	
	R.: a methyl or ethyl group,	
	R <sub>s</sub> : a methyl or ethyl group,	5
5	R <sub>i</sub> : a hydrogen atom, R <sub>i</sub> : a carbalkoxy group, a carbalkoxyalkyl group, a 3,4-methylenedioxyphenyl group, R <sub>i</sub> : a carbalkoxy group, a carbalkoxyalkyl group, a 3,4-methylenedioxyphenyl group,	J
	of a group having the general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11, wherein 2 is the care of a land general formula 11 is the care of a land general for a land general formula 11 is the care of a land general formula 11 is the care of a land general formula 11 is the care of a	
	-40m m in word of and grat x 19 L M. Walta in 12 Diff.	
	7. A novel compound corresponding to the general formula 1 in claim 1, in which	
10	the symbols have the following meanings:	10
•	A: a hydrogen atom,	
	B: a hydrogen atom, C: a hydrogen atom, and	
	D. a hydrogen street of	
15	CD: when taken together, a further single bond between the adjacent carbon atoms,	15
13	n: zero of one,	-
	m: zero or one,	
	R <sub>s</sub> : a methyl or ethyl group,	
20	R <sub>s</sub> : a methyl or ethyl group, R <sub>s</sub> : a hydrogen atom,	20
20	p. a carbolkovy group, a carbalkovyalkyl a 3.4-methylenedioxyphenyl group, or a	
	group having the general formula 11, wherein Z is CH of a indogen atom, p	
	is zero or one, and X is CH <sub>2</sub> , when p is one.	
	8. A compound according to claim 1 or claim 2, which is benzaldoxime-O-geranyl	25
25	ether.  9. A compound according to claim 1, or claim 2 which is benzaldoxime-O-6,7-	23
	10. A compound according to claim 1 or claim 2, which is benzaldoxini-0-(/	
	-there are not better	30
30	11. A company 1 and according to claim 1 or claim 2, which is benzaldoxime-O-(3-	30
	ethyl-7-methyl-2,6-nonadiene-1-yl)-ether.  12. A compound according to claim 1 or claim 2, which is piperonaloxime-O-	
	annual other	
	13. A compound according to claim 1 or claim 2, which is p-total according to claim 1 or claim 2, which is p-total according to claim 1 or claim 2, which is p-total according to claim 1 or claim 2, which is p-total according to claim 1 or claim 2, which is p-total according to claim 2.	
35		35
	14. A compound according to claim 1 or claim 2, which is 3-pyridinealdoxime-O-	
	geranyl ether.  15. A compound according to claim 1 or claim 2, which is benzaldoxime-O-citro-	
	andly Lathor	45
40	16. A compound according to claim 1 or claim 2, which is pre-consistence—(5-	40
	methyl-2-pentene-1-yl)-ether.  17. A compound according to claim 1 or claim 2, which is benzaldoxime-O-(3-	
	methyl-2-pentene-1-yl)-ether.	
	18. A compound according to claim 1 or claim 2, which is piperonaloxime-O-(4-	
45	marked 2 howard 1 vi \ether	45
•••	19. A compound according to claim 1 or claim 2, which is benzamus. 0-(1-	
	methyl-3-hexene-yl)-ether.	
	20. A compound according to claim 1 or claim 2, which is glycollicaldoxime-O-	
EΛ	geranyl ether.  21. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester	50
50	aldonima A gommyl ether	•
	22. A compound according to claim 1 or claim 2, which is gryoxylic acid enlysester	
	aldoxime-O-(epoxygeranyl)-ether.	
	23. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(7-ethoxy-geranyl)-ether.	55
5 <b>5</b>	24. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester	
	aldanima () airmaelly ather	
	25. A compound according to claim 1 or claim 2, which is gryoxyne acid editiested	
	aldering O. (7-methovy-citmuelly) -ether.	60
60	26. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(3,7-dimethyl-octyl)-ether.	•
	27. A process of preparing a chemical compound of the general formula I as	
	defined in claim 1, in which	
	a) a compound of the general formula III	
	· · · · · · · · · · · · · · · · · · ·	

is reacted with a compound of the formula IV

IV

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preferably in the presence of a base, in which formulae A, B, C, D, n, m, R, R, and R, have the same meaning as indicated in claim 1, and Hal is a halogen atom, preferably a chlorine, bromine or iodine atom, or

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b) a compound of the general formula IIIb

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IIIbb

is epoxidized to form a compound of the general formula IIIbb

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5

10

which is then reacted with a compound of general formula IV, according to process a), to form a compound of general formula Ib

IР

in which formulae C, D, n, m,  $R_a$ ,  $R_a$ ,  $R_a$ ,  $R_a$  and Hal have the above meaning, or c) a compound of the general formula IIIb, indicated above, is alkoxylated to form a compound of the general formula IIIc

15

IIIc

Ic

which is then reacted with a compound of general formula IV, according to process a), to form a compound of general formula Ic

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$$\left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ R_{m} \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\ \\ \\ \end{array} \right\} = \left\{ \begin{array}{c} R_{m} \\ \\$$

20

in which formula C, D, n, m, R, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and Hal have the above meaning, and R<sub>4</sub> is an alkyl group having from 1 to 6 carbon atoms.

28. A process as claimed in claim 27a), in which the reaction is performed in the

presence of a base and in an organic solvent, preferably potassium hydroxide or sodium hydride in dimethylformamide.

25

	29. A process as claimed in claim 27b), in which the epoxidation is carried out with m-chloroperbenzoic acid as the epoxidation agent.  30. A process as claimed in claim 27c), in which the compound of formula IIIb is	
	reacted with a mercuric salt in an alcohol of formula R.OH, wherein R, has the mean-	_
5	ing stated in claim 27c), and the resulting oxymercuric intermediate product is reduced to form the compound of formula IIIc.	3
	31. A process as claimed in claim 30, in which the reduction of the oxymercuric intermediate is performed by means of NaBH, in aqueous sodium hydroxide.	
	32. A process of preparing a chemical compound of general formula I as defined	
10	in claim 1, substantially as described, with special reference to the Examples 1 to 3 and	10
•	to the variation stated on pages 6-7.	
	33. A composition for the control of insects, which comprises a compound of the	
	general formula I, as defined in any of the claims 1 to 6 together with a carrier for said	
	compound.	15
15	34. A composition according to claim 33, which as an active ingredient contains a compound as stated in any of the claims 8 to 26.	13
	35. A composition for the control of insects, substantially as described, with special	i
	reference to Example 5.	
	36. A method for the control of insects which comprises contacting insects, or their	
20	eggs or larvae with a composition as claimed in any of the claims 33 to 35.	20
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